CHAPTER 6

Alternative Disinfectants[1]

Introduction

Chlorination of drinking water results in the formation of numerous disinfection byproducts (DBPs), several of which are regulated. Water systems seeking to meet maximum contaminant levels (MCLs) of regulated DBPs may consider various approaches to limiting DBPs: removing the precursor compounds early in the treatment train before the disinfectant is applied, using less chlorine, using alternative disinfectants to chlorine, and removing DBPs after their formation. Combinations of these approaches may also be considered. Removing DBPs after their formation is a method that is generally not employed. Whatever approach is selected, the system must be certain that the effectiveness of the disinfection is not jeopardized. This chapter presents recent studies conducted by, or funded by, the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development (ORD) in Cincinnati that examine the use of three alternative oxidants: chloramine, chlorine dioxide, and ozone.

Models for Assessing Halogenated DBP Precursors

The precursors for halogenated DBP formation are not well known. In the Disinfectants/Disinfection By-Product (D/DBP) Rule, in which enhanced coagulation is used as a treatment technique to control identified and unidentified DBPs, total organic carbon (TOC) is the surrogate for DBP precursors. While TOC or dissolved organic carbon (DOC) may be used as a surrogate, they will not well represent the precursors of specific DBPs. While the precursors for the specific DBPs are not well known, an indirect means of quantitating the control of specific DBP precursors is to sample the water influent to and effluent from a treatment process, chlorinate both waters under a specific set of conditions (pH, temperature, time, etc.), and examine the concentrations of the specific DBPs. Differences in these concentrations may be attributed to the effectiveness of the treatment process. For example, a raw water may form 200 mg/L of total trihalomethane (TTHM), while an ozonated water may form 150 mg/L. Ozonation may then be considered to have oxidized 25% of the TTHM precursors. The set of chlorination conditions driving the DBP reaction is very important. Three models for DBP precursor were employed in the studies discussed in this chapter.

In the formation potential (FP) model, a relatively large dose of chlorine is used, and the reaction time is typically long, e.g., one week. This is assumed to drive the DBP reaction to completion, thus utilizing all the precursor. The fate of precursors can be assessed across treatment processes, but, as conditions are relatively extreme, the resulting DBP concentrations are rarely representative of a system's finished water.

Systems may therefore choose to chlorinate under conditions unique to their distribution system. In the simulated distribution system (SDS) model, the fate of precursors can be assessed; the resulting DBP concentrations are representative of the system's finished water. For example, SDS TTHM concentrations before and after biological filtration may be 85 and 70 μg/L, respectively. The biofilter is shown to remove 17% of the TTHM precursor. The 70 μg/L is meaningful, as the chlorination conditions were

representative. The 70 µg/L is below the Stage 1 D/DBP Rule MCL of 80 µg/L. If FP conditions were used, the TTHM formation potential (TTHMFP) concentrations before and after biological filtration might have been 140 and 116 µg/L, respectively. The biofilter would show 17% removal of the TTHM precursor, but as chlorination conditions were not representative, the 116 µg/L would incorrectly imply that the MCL was exceeded. Additionally, the use of the FP model might result in a skewed distribution of bromo- and chloro-trihalomethanes (THMs). The chlorine-to-bromide ratio impacts DBP speciation (Shukairy et al. 1994), and this ratio is typically higher when the FP model is employed.

Because chlorination conditions are unique to the systems employing them, the SDS model does not allow for comparison of results from different waters. The uniform formation condition (UFC) model was developed to address this issue (Summers et al. 1996). In this model, the chlorination conditions of the mean national distribution system are targeted, i.e., 1 mg/L free-chlorine residual at 24 hours at pH 8 at 20°C. Thus, DBP precursor control can be assessed, the resulting DBP concentrations can be considered relative to MCLs, and results can be compared from one water to another.

Chloramines

Chloramines are the second most commonly used final disinfectant in drinking water treatment after free chlorine. Although generally not as effective a disinfectant as free chlorine, an advantage of chloramination is minimization of the formation of DBPs.

Halogenated DBP Formation

The formation of DBPs by chloramines is significantly lower than by free chlorine. Stevens et al. (1989) treated humic acid solutions with free chlorine, monochloramine, and chlorine dioxide at the bench-scale. Monochloramine was dosed as preformed chloramines without free chlorine. The solutions contained no bromide, so only chloro-DBPs resulted. Figure 6-1 shows the relative formation of $CHCl_3$ and nonpurgable organic halide (NPOX), a subset of the surrogate total organic halide (TOX). The data show that $CHCl_3$ formation and NPOX formation by monochloramine is small compared to that formed by free chlorine, confirming that a treatment strategy for the control of DBPs is the use of chloramines as an alternative final disinfectant to free chlorine.

Parallel oxidants were studied at the pilot scale in Jefferson Parish, LA, treating Mississippi River (MR) water (Lykins and Koffskey 1986; Lykins et al. 1989). Coagulated, settled, and filtered waters were treated with free chlorine, monochloramine, chlorine dioxide, and ozone and compared to a parallel nondisinfected water. Results for TOX formation representing the mean of one year of sampling are listed in Table 6-1. Disinfectant contact times averaged 31 minutes. No details were given regarding how monochloramine was prepared or dosed. The TOX formation by monochloramine, however, was low compared to that by free chlorine.

At the pilot-scale, Miltner (1990) studied chlorination and chloramination of Ohio River (OR) water. Parallel plants were predisinfected, alum-coagulated to control turbidity, settled, and filtered. In the

Table 6-1. Oxidation of MR Water (Lykins and Koffskey 1986)

Parameter	Disinfectant				
	None	Free Chlorine	Monochloramine	Chlorine Dioxide*	Ozone
Residual, mg/L		1	2.1	0.5	0.5
TOX, µg Cl⁻/L	25	263	117	85	15

* Chlorite = 0.6 mg/L, free chlorine = 0.1 mg/L
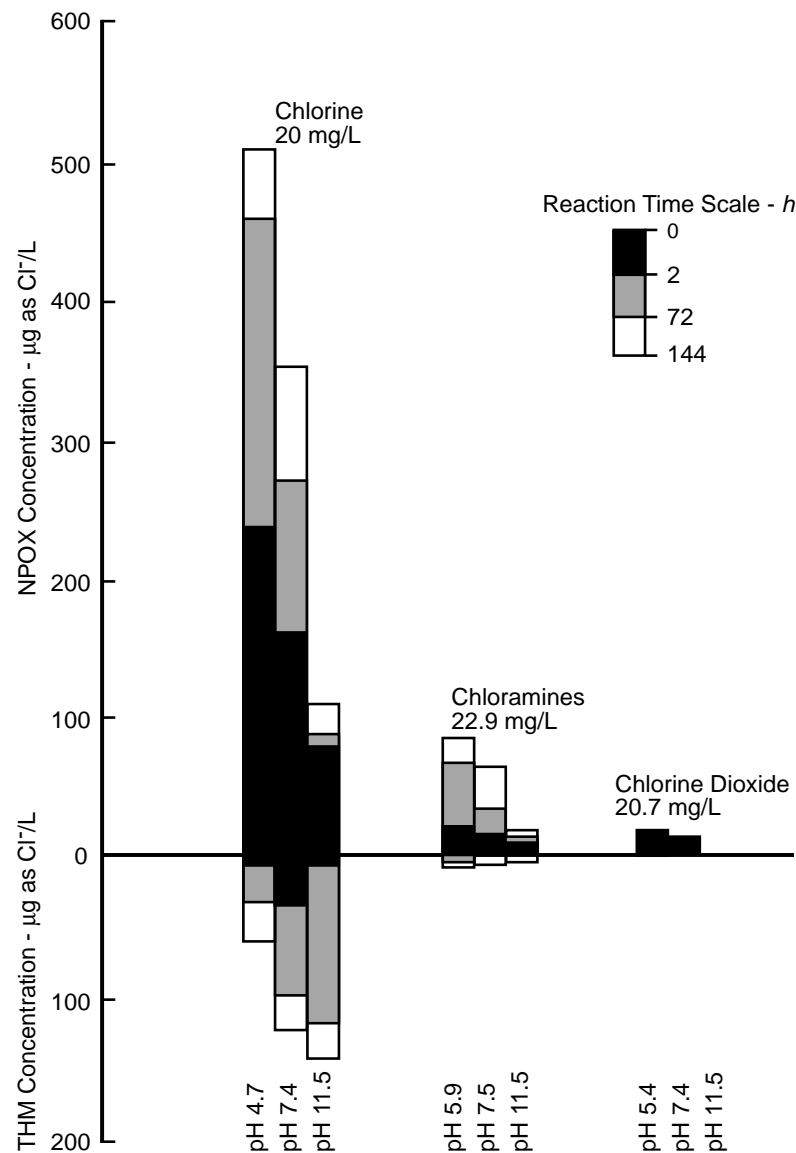
Figure 6-1. Formation of DBPs by alternative oxidants (Stevens et al. 1989).

chloramine plant, NH_4OH was added in stoichiometric excess before rapid mix; no free chlorine was present. Chlorine was added to the rapid mix in both plants. Chlorine was dosed on both plants so that residuals carried through the filters and clear wells and met the Ten-State Standards (TSS) (Recommended Standards for Water Works 1992) of 0.2 to 0.5 mg/L free chlorine and 1.0 to 2.0 mg/L combined chlorine "at distant points in the distribution system." In this study, the distribution system was simulated as clear well waters held 3 days. Table 6-2 shows results for mean sampling of clear well effluents. HAN4 represents four haloacetonitriles (HANs): trichloro- (TCAN), dichloro- (DCAN), bromochloro- (BCAN) and dibromo- (DBAN). Chloropicrin (CP) was not detected. Cyanogen chloride, chloral hydrate (CH), and the haloacetic acids (HAAs) were not analyzed.

THMs, HANs and 1,1,1-trichloropropanone (111-TCP) were detected in the finished water on the prechlorinated plant. As expected, these DBPs were not detected in the finished water on the prechloraminated plant. The TOX concentration was appreciably lower in the effluent of the prechloraminated plant and similar in concentration to the TOX concentration in the OR water influent to the plant.

Table 6-2. DBP Formation in Finished OR Water (Miltner 1990)

Parameter	Concentration, µg/L	
	Prechlorinated	Prechloraminated
TOX	115	20
TTHM	15.6	ND
$CHCl_3$	10.0	ND
$CHBrCl_2$	4.6	ND
$CHBr_2Cl$	0.7	ND
$CHBr_3$	0.3	ND
HAN4	3.1	ND
TCAN	3.1	ND
DCAN	<0.1	ND
BCAN	ND	ND
DBAN	ND	ND
111-TCP	2.8	ND
CP	ND	ND

ND = not detected

Although bacteria penetrated farther into the chloraminated plant, heterotrophic plate count (HPC) and total coliform (TC) densities were comparable in the two finished waters, indicating that chloramination following the TSS was sufficient for bacterial control.

On the same pilot plant, Miltner et al. (1990) studied parallel post-chlorination and post-chloramination of OR water following preozonation, alum coagulation to control turbidity, and settling. Following settling, the stream was split for parallel filtration. Following filtration, the post-disinfectants were applied to the clear well influents. For monochloramine, NH_4OH was added in stoichiometric excess prior to chlorine; no free chlorine was present. A parallel plant without preozonation was similarly treated with post-chlorination at the clear well's influent. Finished waters collected from clear wells and held 3 days were used to simulate distribution system waters. Residuals targeted recommendations of the TSS (Recommended Standards for Water Works 1992); residuals after 3 days were near 0.2 mg/L free chlorine and 0.7 mg/L monochloramine. Results are given in Table 6-3. HAA6 represents six HAAs: trichloro- (TCAA), dichloro- (DCAA), chloro- (CAA), bromochloro- (BCAA), bromo- (BAA), and dibromoacetic acid (DBAA).

Comparing ozone/chloramine and ozone/chlorine, the concentrations of 3-day DBPs were significantly lower with use of monochloramine, as expected. TOX was also formed upon chloramination, but at significantly lower concentrations than in the chlorinated waters and only near double the raw water TOX concentration of 24.4 µg Cl⁻/L. The only noted exception in DBP formation was the formation of cyanogen chloride upon chloramination.

The THMs, HAAs, HANs, CH, CP, 111-TCP and CNCl concentrations in Table 6-3 were converted to their TOX equivalents and compared to their TOX concentrations. In the two chlorinated waters, these DBPs accounted for nearly 40% of the TOX, leaving nearly 60% of the TOX unaccounted for, i.e., 60% of the TOX was comprised of compounds other than these DBPs. In the chloraminated water, however, these DBPs made up only 23% of the TOX. Thus, the use of chloramine resulted in significantly lower DBP formation than the use of free chlorine (refer to Table 6-3), but a larger percentage of what was formed was unaccounted for by the measured DBPs. This unaccounted-for, halogenated material may be nitrogenous.

Table 6-3. DBP Formation in Simulated Distribution OR Water (Miltner et al. 1990)

Parameter	Concentration, µg/L Unless Noted			T-Test* for Chlorinated Waters		
	O_3 Chloramine	O_3 Chlorine	Post Chlorine	Better With O_3	Same	Better Without O_3
TOX, µg Cl⁻/L	51.5	207	259	×		
TTHM	5.6	75.1	90.4	×		
CHCl₃	4.5	39.6	55.5	×		
CHBrCl₂	0.8	21.1	24.4		×	
CHBr₂Cl	0.2	13.0	10.2			×
CHBr₃	ND	1.5	0.3			×
HAA6	6.1	39.7	62.6	×		
TCAA	1.5	10.0	20.1	×		
DCAA	3.9	19.2	30.9	×		
BCAA	0.3	6.8	8.5	×		
CAA	0.5	1.5	1.4	×	×	
BAA	<0.1	0.3	0.3		×	
DBAA	ND	2.0	1.5			×
HAN4	2.9	4.8	5.7		×	
TCAN	ND	ND	0.2		×	
DCAN	2.4	2.6	3.5		×	
BCAN	0.4	1.7	1.9		×	
DBAN	0.2	0.6	0.1			×
CH	0.8	5.8	4.2			×
CP	0.1	1.6	0.5			×
111-TCP	0.4	1.1	0.8		×	
CNCl	2.5	ND	ND			

    * at 95% confidence level

  ND = not detected

Comparing ozone/chloramine and ozone/chlorine, the densities of HPC in the two clear wells were similar. TC bacteria were not detected in any clear wells. These data suggest that chloramination following the recommendations of the TSS was sufficient for bacterial control. With this pilot-scale study and the pilot-scale study noted previously, water distribution system materials could not be simulated during the 3-day storage of chlorinated water in clean glassware; therefore, the question of bacterial regrowth in the presence of the weaker chloramine disinfectant during distribution remains.

Nonhalogenated DBP Formation

The formation of nonhalogenated DBPs by chloramines is also significantly lower than by free chlorine. Miltner (1993) reported on OR water at the bench-scale with several oxidants. With monochloramine, the formation of formaldehyde and the P17 strain of assimilable organic carbon (AOC-P17) was negligible and similar to the background concentrations. With free chlorine, however, formaldehyde and AOC-P17 formation was evident (see Table 6-4). The data suggest that systems employing monochloramine will experience lower concentrations of these bacterial nutrients in their distribution systems than those employing free chlorine.

Table 6-4. Oxidation of OR Water (Miltner 1993)

Oxidant	Dose, mg/L	Time, min	Formaldehyde, μg/L	AOC-P17, μg Ceq/L*
None			0.8 ± 0.15	95
Monochloramine	2	15	0.9	96
ClO_2	1	15	2.0	129
$KMnO_4$	1	15	2.2 ± 0.85	132
Free chlorine	3	15	2.8	158
Ozone	2	7.5	17.1	202

*as acetate

Chlorine Dioxide

Chlorine dioxide is a widely used disinfectant in drinking water treatment. It has long been used for taste and odor control and for iron and manganese control and has gained in acceptance as an effective disinfectant. An advantage of ClO_2 treatment is minimization of the formation of DBPs; it does this by oxidation of DBP precursors and by relatively minimal formation of DBPs themselves. A disadvantage is the presence of chlorite and chlorate resulting from ClO_2 treatment. The former is regulated under the D/DBP Rule and the latter is of health concern.

Halogenated DBP Formation

The formation of DBPs by chlorine dioxide is significantly lower than by free chlorine. Stevens et al. (1989) treated humic acid solutions with free chlorine, monochloramine, and chlorine dioxide at the bench-scale. The solutions contained no bromide, so only chloro-DBPs resulted. Figure 6-1 shows the relative formation of $CHCl_3$ and NPOX. The data show no $CHCl_3$ formation and little NPOX formation by chlorine dioxide compared to that formed by free chlorine. Thus, a treatment strategy to control DBPs is the use of chlorine dioxide, an alternative oxidant to free chlorine.

Table 6-1 shows that TOX formation by ClO_2 on the Jefferson Parish pilot plant was low compared to that of free chlorine. Some of the TOX in the ClO_2-treated water may be a result of inefficient ClO_2 generation, as a yearly average free chlorine residual of 0.1 mg/L was detected following ClO_2 contact.

The effect of ClO_2 on TTHM control was observed by Lykins and Griese (1986) at Evansville, IN. Pilot-plant effluents (no prior disinfection) were treated with chlorine and ClO_2 and held 3 days to simulate distribution system conditions. Results are presented in Table 6-5. Even with a high ClO_2 residual and 3 days' reaction time, TTHM formation was similar to the background TTHM concentration in the raw water and very low compared to the formation by free chlorine.

Based on the success of piloting, a full-scale switch to ClO_2 was made at Evansville. Evansville has two parallel full-scale plants. One was treated with ClO_2 as a preoxidant, with an average dose of 1.4 mg/L ClO_2. Both plants were chlorinated ahead of the filters. No details were given on the free-chlorine doses to the two plants or whether the free chlorine dose on the ClO_2-treated plant may have been lower as a

Table 6-5. TTHM Formation at Evansville (Lykins and Griese 1986)

Parameter	Simulated Distribution Concentrations	
	Chlorine	Chlorine Dioxide
TTHM, μg/L*	141	1.4
Chlorine residual, mg/L	2.5	—
Chlorine dioxide residual, mg/L	—	1.9

* TTHM in raw water = 1.2 μg/L.

result of ClO_2 satisfying some of the chlorine demand. Nevertheless, pretreatment with ClO_2 was effective in lowering TTHM formation (Lykins and Griese 1986). Finished water TTHM averaged 37.3 mg/L without ClO_2 and 25.5 mg/L with ClO_2. There are two explanations for this improvement. Lykins and Griese (1986) hypothesized that lower TTHM concentrations were a result of ClO_2's oxidation of DBP precursor prior to downstream chlorination. Miltner (1976) showed that ClO_2 oxidized DBP precursors to the extent that lower concentrations of DBPs were formed with subsequent chlorination. The second explanation contends that, if the free chlorine level was lower on the ClO_2-treated plant as a result of ClO_2's oxidation of chlorine demand, lower TTHM may also result.

The effect of ClO_2 on DBP precursors was also studied by Lykins and Koffskey (1986) at the pilot scale at Jefferson Parish. Coagulated, settled, and filtered waters were treated with free chlorine, chlorine dioxide, and ozone. TTHM and TOX precursors were assessed by FP. Table 6-6 shows ClO_2 oxidized 34% and 17%, respectively, of TTHM and TOX precursors.

Table 6-6. Oxidation of DBP Precursors at Jefferson Parish (Lykins and Koffskey 1986)

| Parameter | Percent Removal | |
	Chlorine Dioxide	Ozone
TTHMFP	34	44
TOXFP	17	31

Nonhalogenated DBP Formation

While the formation of halogenated DBPs by chlorine dioxide may be minimal compared to free chlorine, ClO_2 can form nonhalogenated by-products. Miltner (1993) reported on OR water at the bench-scale with several oxidants. With chlorine dioxide, the formation of formaldehyde and AOC-P17 approached that of free chlorine (see Table 6-4).

EPA (unpublished data) sampled a full-scale plant treating OR water with $KMnO_4$ and ClO_2. The ClO_2 dose was near 1.0 mg/L. Results in Table 6-7 show the presence, confirmed by chromatograph/mass spectroscopy (GC/MS), of aldehydes and ketones in ClO_2-treated water. While the presence of these compounds in the ClO_2-treated water may also be a result of their presence in the source water and/or the result of $KMnO_4$'s ability to form them (refer to Table 6-4), the concentration of several of them was enhanced by ClO_2 treatment.

Table 6-7. Aldehyde/Ketone Formation in OR Water

| Parameter | Concentration, µg/L | |
	$KMnO_4$ Treated Raw	ClO_2 Treated Mixed
Formaldehyde	10.1	10.8 C
Acetaldehyde	11.2	24.1 C
Propanal	1.5	25.1 C
2-Butanone		25.1 C
Butanal	2.6	40.6 C
Pentanal		C
2-Hexanone		C
Hexanal	1.6	16.2 C
Octanal		C
Benzaldehyde		C

C = GC/MS confirmed

Richardson et al. (1994) utilized XAD® resin extraction and GC/MS to qualitatively search for by-products in waters taken from a pilot plant in Evansville, IN, employing ClO_2. They identified 20 compounds in ClO_2-treated water that were not identified in the raw water. Most were carboxylic acids in the C4 through C16 range. A few ketones were also identified.

Controlling Concentrations of Chlorine Dioxide, Chlorite, and Chlorate

Chlorite and chlorate are found in ClO_2-treated waters. They may result from unreacted ClO_2 generator products, the reduction of ClO_2, or the disproportionation of ClO_2 and its related products. Table 6-1 shows chlorite measured in ClO_2-treated waters at Jefferson Parish. As both chlorite and chlorate have toxicological implications, as the D/DBP Rule regulates chlorite in drinking water, and as the D/DBP Rule limits the allowable concentration of ClO_2 in finished waters, the control of all three species is important to systems employing ClO_2.

Granular activated carbon (GAC) with an empty bed contact time of 9.6 minutes was studied at the Evansville pilot plant for control of ClO_2 and chlorite (Lykins et al. 1990; Lykins et al. 1989). Results are given in Table 6-8. They show that much of the ClO_2 is reduced to chlorite downstream of its application, that ClO_2 was completely reduced before entering the GAC bed so its control by GAC could not be evaluated, and that a substantial percentage of the chlorite was controlled by GAC. Chlorite control by GAC would very likely be time dependent; no details were given as to GAC age, bed volumes treated, etc.

Table 6-8. Control of ClO_2 and ClO_2^- at Evansville (Lykins et al. 1990)

	Chlorine Dioxide, mg/L	Chlorite, mg/L
Dose	4.2	
Settled	0.5	2.3
GAC influent	ND	3.0
GAC effluent	ND	0.3

ND = not detected

Griese et al. (1991) studied the use of reducing agents to control ClO_2 and chlorite at the bench scale at Evansville. Applying excess sulfur dioxide and sulfite was found to remove both ClO_2 and chlorite. SO_2/SO_2^- was most efficiently applied after the oxidant demand for ClO_2 had been met. The reaction, in part, depended on the dissolved oxygen (DO) concentration. Using this means of control, unreacted SO_2/SO_2^- would complicate post-disinfection. They assumed unreacted SO_2/SO_2^- would be removed by post-chlorination, but require a higher post-chlorine dose than would otherwise be required. This means of control was not pursued, however, since unacceptable concentrations (exceeding 1 mg/L) of chlorate were formed. They found similar results with the application of excess metabisulfite. Results with excess thiosulfate were more promising. It controlled both ClO_2 and chlorite, was pH and time dependent, was not affected by DO, and did not form complicating concentrations of chlorate. But it would also pose a problem for finished waters, as unreacted thiosulfate would complicate post-disinfection.

Griese et al. (1991) also studied ferrous chloride at the pilot scale at Evansville. They found this to be the most promising reducing agent as it controlled both ClO_2 and chlorite and formed only very low concentrations of chlorate. Residual iron was controlled with prefilter chlorination. Other studies by Griese et al. (1992) at the pilot scale expanded on ferrous iron as a means of control and focused on chlorate. They found chlorate could be present as a product of the ClO_2 generation process, as a result of ClO_2's reaction with sunlight, and as a result of uncontrolled ClO_2 and chlorite reacting with post-chlorine. They found that chlorate formation during ferrous iron treatment was higher at lower pH and that adding lime to a pH range of 7.0 to 7.5 minimized chlorate formation.

Ozone

Ozone is a less commonly used disinfectant in drinking water treatment. Among the many benefits of ozonation of drinking water are effective inactivation of microbes, taste and odor control, iron and manganese control, oxidation of DBP precursors, and the enhancement of biological oxidation in filters. However, ozone results in the formation of bromate and of biodegradable organic matter (BOM). Bromate is regulated under the D/DBP Rule. BOM includes ozone by-products (OBPs) like aldehydes, keto acids, carboxylic acids, AOC, and biodegradable dissolved organic carbon (BDOC). These OBPs may be responsible for regrowth of bacteria in distribution systems and can be controlled in-plant if biological oxidation is allowed to occur in downstream filters. (Refer to Chapter 7, "DBP Control Through Biological Filtration.")

Halogenated DBP Formation

The formation of halogenated DBPs as a result of ozonation is minimal. EPA unpublished data showed the low-level formation of brominated DBPs by ozone in the conduct of pilot-scale studies (Miltner et al. 1990; Miltner and Summers 1992) of OR water. $CHBr_3$, BAA, and DBAA were occasionally detected at concentrations below 2 µg/L, presumably through the reaction of molecular ozone, bromide, and natural organic matter (NOM). Downstream chlorination significantly increased the concentrations of these DBPs.

Table 6-1 describes TOX concentrations as a result of ozonation of MR water at the Jefferson Parish pilot plant. A 31-minute contact time resulting in a 0.5-mg/L ozone residual did not increase TOX concentrations beyond those in the background water.

Oxidation of Halogenated DBP Precursor

DBP precursors tend to be more humic than non-humic and of higher rather than lower molecular weight. In Chapter 10, Coagulation, Dryfuse et al. (1995) describe TOX, TTHM, and HAA6 precursors located predominantly in the humic and higher-molecular-weight fractions of East Fork Lake (EFL) water. Koechling et al. (1996), studying the reaction of ozone with NOM, found that ozone converted portions of the humic fraction to non-humic compounds and converted portions of the higher-molecular-weight fraction to lower-molecular-weight compounds. Therefore, ozone reacts with NOM to oxidize a portion of the DBP precursors; this results in lower concentrations of DBPs formed by downstream chlorination. Coupled with the low-level formation of bromo-DBPs by ozone itself, this finding supports ozone's role as an alternative oxidant for halogenated DBP control.

Tables 6-9 and 6-10 describe ozone's oxidation of DBP precursor in pilot-scale studies of OR water and EFL water, respectively. In the OR water study (Table 6-9), ozone was applied to raw OR water at a transferred ozone/TOC ratio near 0.8 mg/mg. Miltner et al. (1992) studied ozone dose dependency and demonstrated with pilot-scale ozonation of OR water that, at transferred ozone/TOC ratios above 0.7 mg/mg, no further oxidation of TTHM, HAA6, and TOX precursors occurred. While ozone changed the nature of the DOC (to more non-humic and to smaller-molecular-weight compounds), it did not significantly change its concentration, as Table 6-9 demonstrates. Ozone significantly oxidized compounds that absorb at 254nm (UV254) and consequently lowered the water's specific ultraviolet (UV) absorbance (SUVA), or UV254 divided by DOC. Using FP as a means of assessing DBP precursors, removal of TTHM, HAA6, and TOX precursors by ozone was within the 14% to 19% range. However, ozone altered the nature of CH and CP precursors to the extent that they increased.

In the EFL water study, ozone was applied to coagulated and settled EFL water at a transferred ozone/TOC ratio near 0.9 mg/mg. Table 6-10 shows the removal of DBP precursors first by coagulation and

Table 6-9. Mean Changes in DBP Precursors in Ozonated OR Water (Miltner 1993)

Parameter	Raw	Ozonated	Percent Removal
DOC, mg/L	2.28	2.24	
UV254, cm^{-1}	0.051	0.027	47
SUVA, L/mg-m	2.23	1.20	46
TTHMFP, μg/L	190	164	14
HAA6FP, μg/L	155	126	19
TOXFP, μg Cl$^-$/L	449	367	18
CHFP, μg/L	33	40	+21
CPFP, μg/L	1.5	2.9	+93

Table 6-10. Mean Changes in DBP Precursors in Ozonated EFL Water (Miltner et al. 1996)

Parameter	Raw	Coagulated Settled	Coagulated Settled, Ozonated	Percent Removal by Ozonation
DOC, mg/L	5.83	2.77	2.74	
UV254, cm^{-1}	0.204	0.068	0.023	66
SUVA, L/mg-m	3.50	2.12	0.84	60
UFC TTHM, μg/L	311	83.6	48.7	42
UFC HAA6, μg/L	332	79.1	52.5	34
UFC TOX, μg Cl$^-$/L	984	300	210	30
UFC CH, μg/L	32.2	11.4	18.3	+61
UFC HAN4, μg/L	12.6	6.9	3.6	48
Chlorine demand, mg/L	9.27	3.04	2.86	6

then by ozonation. Precursors were assessed by UFC. Again, ozone did not affect the DOC concentration, but removed SUVA, chlorine demand, and TTHM, HAA6, HAN4, and TOX precursors. Precursors for CH were increased by ozone oxidation.

Ozone oxidation of TTHM and TOX precursors was also observed by Lykins and Koffskey (1986) in pilot-scale Jefferson Parish waters (see Table 6-6).
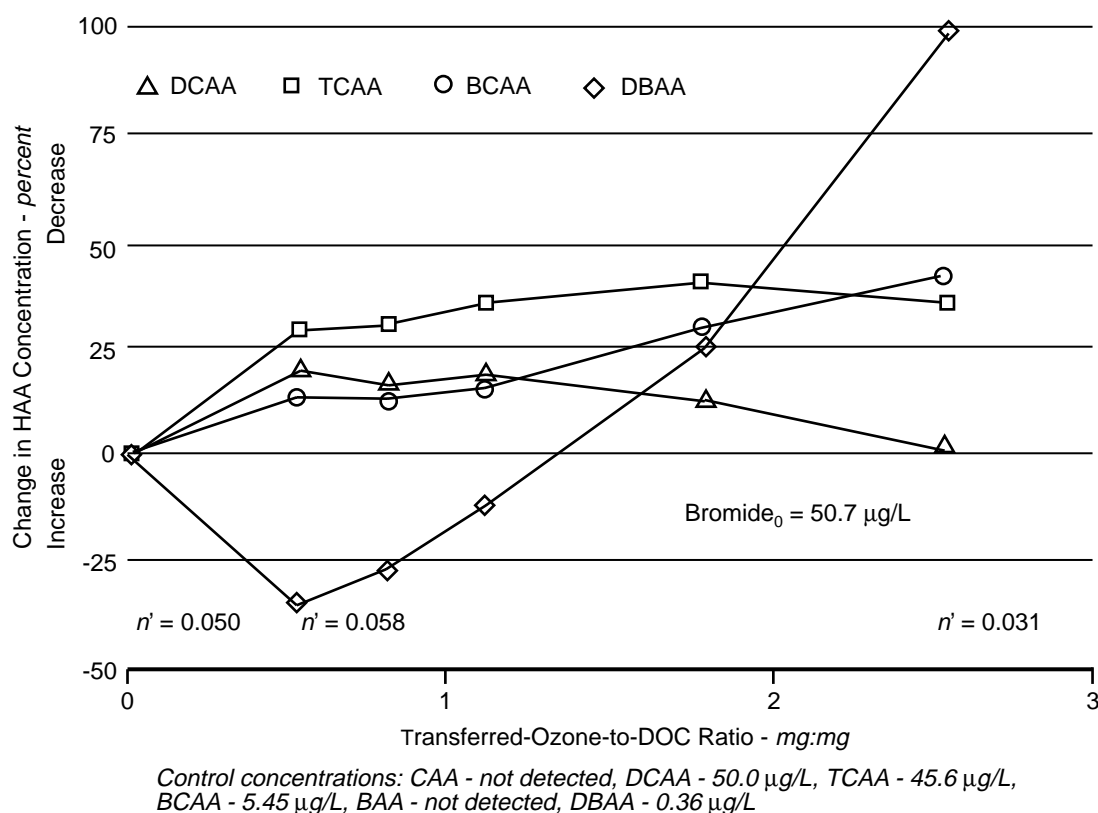
Results of another pilot-scale study of ozonation of raw OR water (Miltner et al. 1990) are presented in Table 6-3. A preozonated/post-chlorinated stream was compared to a stream that was post-chlorinated only. Post-chlorination was conducted under SDS conditions of 3-day chlorination targeting TSS chlorine residuals (Recommended Standards for Water Works 1992). The data show lower concentrations of finished water TTHM, HAA6, HAN4, and TOX in the preozonated stream. Two factors account for this: (1) preozonation removed a portion of the precursors by oxidation, and (2) preozonation lowered the chlorine demand so that less chlorine was applied and was present to drive DBP formation. Exceptions were finished water concentrations of CH, CP, and 111-TCP, the precursors of which were increased by preozonation.

Table 6-3 shows a statistical test of the two chlorinated finished waters, showing 95% confidence in the lower concentrations of TOX, TTHM, CHCl$_3$, HAA6, TCAA, DCAA, and BCAA when preozonated, and showing 95% confidence in the higher concentrations of CHBrCl$_2$, CHBr$_3$, DBAA, DBAN, CH, and CP when preozonated. Ozone's increase of CH and CP precursors has been previously noted. Ozone's effect on the bromochlorospeciation of halogenated DBPs is just as, if not more, important.

Shukairy et al. (1994) studied ozone's oxidation of DBP precursors in OR water and the resulting bromochlorospeciation. DBP precursors were assessed by chlorinating under FP conditions. Figure 6-2 shows representative results for individual HAAs. Oxidation of precursors for TCAA, DCAA, and BCAA occurred to the extent that, over the range of transferred ozone/DOC ratios up to 2.54 mg/mg, their concentrations decreased upon chlorination. This is consistent with the behavior of HAA6 precursors also observed by Miltner et al. (1992), noted previously.

At transferred ozone/DOC ratios at and below 1.11 mg/mg, however, concentrations of DBAA increased. This behavior is consistent with the statistically significant increases in DBAA concentrations presented in Table 6-3 in which ozonation took place at 0.8 mg/mg transferred ozone/TOC. As the ozone increased, however, there was a significant decrease in DBAA formation. At transferred ozone/DOC ratios at and below 1.11 mg/mg, changes in bromide were small. At higher ozone doses, more bromate was formed from bromide (refer to Table 6-15), thus bromide concentrations fell. As a result, the bromide/DOC ratios and the bromide/free-chlorine ratios decreased. Decreases in either ratio favor the formation of more chlorinated species as was observed above 1.11 mg/mg.

Figure 6-2 also shows the bromide incorporation factor n', which is defined as the molar ratio of the brominated HAAs to the total HAA6 (Shukairy et al. 1994). At lower ozone doses, when DBAA concentrations increased, n' increased; at higher ozone doses, when DBAA concentrations decreased, n' decreased. Behavior for THMs was similar with increased concentrations of $CHBr_2Cl$ and $CHBr_3$ and increased n, the bromide incorporation factor for TTHM, at lower ozone doses, and decreased concentrations of these two THMs and n at higher ozone doses. It is important to remember that, although brominated HAAs and THMs in chlorinated waters increase over the range of transferred ozone/DOC ratios common to drinking water treatment, their concentrations are relatively small (below a few ug/L); TTHM and HAA6 concentrations, however, decrease, demonstrating ozone's overall benefit in oxidizing DBP precursors.

Control concentrations: CAA - not detected, DCAA - 50.0 µg/L, TCAA - 45.6 µg/L, BCAA - 5.45 µg/L, BAA - not detected, DBAA - 0.36 µg/L

Figure 6-2. Effect of ozone dose on HAA formation in OR water (Shukairy et al. 1994).

In the studies summarized in Tables 6-3 and Tables 6-9 through 6-13, microbial densities were monitored. Ozonation was always observed to bring TC bacterial densities to less than one colony /100 mL. Ozonation never destroyed all HPC bacteria; they flourished sufficiently in nutrient-rich downstream waters to acclimate biological filters. Post-disinfection with chlorine or chloramine to achieve requirements of the TSS (Recommended Standards for Water Works 1992) lowered finished water HPC levels typically to 2 to 3 log/mL densities.

Ozone By-Product Formation

Ozonation results in the formation of a number of OBPs. Several pilot-scale studies were conducted with transferred ozone/TOC ratios in the 0.8 to 0.9 mg/mg range. Results are presented in Tables 6-11, 6-12, and 6-13. Ozonation of raw OR water over several months (Table 6-11) demonstrated the statistically significant formation of 9 aldehydes and a ketone, principally formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal.

Table 6-11. Mean Formation of Aldehydes and Ketones in Ozonated OR Water (Miltner et al. 1991; Miltner 1993)

	Concentration, μg/L	
Parameter	Raw	Ozonated *
Formaldehyde	1.1	11.7
Methyl glyoxal	0.1	11.4
Glyoxal	1.3	7.6
Acetaldehyde	1.1	3.5
Propanal	1.2	2.1
Hexanal	0.4	1.4
Decanal	0.4	1.1
Nonanal	0.5	1.0
Pentanal	ND@0.2	0.3
2-Butanone	**ND@0.1	0.1

ND = not detected
* Increase with ozone significant at ≥95% confidence level unless otherwise noted.
** Increase with ozone significant at 94% confidence level.

The same pilot study also demonstrated the formation of other OBPs (Table 6-12) over several months' operation: two keto acids, AOC, and BDOC. The aldehydes, ketones and keto acids are small-molecular-weight compounds resulting from ozone's oxidation of the NOM. They are easily biodegradable (assimilable) and are considered to make up portions of the AOC and BDOC. Note that most of these measures of BOM are naturally present in the raw water and are enhanced upon ozonation. The BDOC made up 17% of the DOC in the raw water and was enhanced to 32% following ozonation. Total AOC (the P17 and the NOX fractions) made up 7% of the raw water DOC and was enhanced to 30% following ozonation. Because these OBPs are, by definition, assimilable and biodegradable, they can serve as substrates for bacterial regrowth in distribution systems if not controlled by biological filtration (refer to Chapter 7, "DBP Control Through Biological Filtration").

The nature of the NOM can influence OBP formation. In OR water (Table 6-12) with a DOC concentration of 2.28 mg/L, BDOC and total AOC reached concentrations of 0.71 mg/L and 665 μg Ceq/L, respectively, with transferred ozone/TOC near 0.8 mg/mg. Following coagulation and sedimentation of EFL water, DOC was lowered to a concentration of 2.77 mg/L. With transferred ozone/TOC near 0.9

Table 6-12. Mean Formation of AOC, BDOC, and Keto Acids in Ozonated OR Water (Miltner 1993)

Parameter	Raw	Ozonated [#]
DOC, mg/L	2.28	2.24
BDOC, mg/L	0.39	0.71
AOC-P17, µg Ceq/L*	37	71
AOC-NOX, µg Ceq/L**	129	594
Glyoxylic acid, µg/L	0.2	34.6
Pyruvic acid, µg/L	0.4	12.4

[#] Increase with ozone significant at ≥95% confidence level except for DOC.
* as acetate
** as oxylate

**Table 6-13. Mean Formation of OBPs in EFL Water (Miltner et al. 1996)**

Parameter	Raw	Coagulated Settled	Ozonated
DOC, mg/L	5.83	2.77	2.74
BDOC, mg/L	1.27	0.53	1.21
Total AOC, µg Ceq/L	399	203	1314
Formaldehyde, µg/L	7.7	NA	21.1
Methyl glyoxal, µg/L	0.2	NA	4.4
Glyoxal, µg/L	0.1	NA	15.1
Glyoxylic acid, µg/L	0.2	NA	46.1
Pyruvic acid, µg/L	0.7	NA	15.6

NA = not analyzed

mg/mg, BDOC and total AOC reached 1.21mg/L and 1314 µg Ceq/L, respectively, or roughly twice that of the OR water at approximately the same DOC and transferred ozone/TOC ratio (Table 6-13). A biological filter treating EFL water would have to be more efficient than one treating OR water to ensure similar distribution system loading of AOC and BDOC.

Ozone concentration can influence OBP formation. Several bench- and pilot-scale studies with ozonation of different batches of OR water examined dose dependency (Shukairy et al. 1992; Miltner et al. 1992; Miltner et al. 1998). Maximum transferred ozone/TOC ratios were in the 2.5 to 2.8 mg/mg range. Generally, much of the formation occurs at lower ozone doses. An example is given in Figure 6-3 for total AOC; at a ratio of 2.5 mg/mg, formation was not yet maximized. Similar behavior of still-increasing formation at higher ratios was also observed for BDOC, glyoxylic acid, and formaldehyde (Miltner et al. 1992; Miltner et al. 1998). Maximized and level formation was observed for acetaldehyde and propanal (Miltner et al. 1992; Shukairy et al. 1992).

Pentanal was found to reach a maximum near 1.8 mg/mg and then diminish in concentration as more ozone was introduced (Shukairy et al. 1992). It is possible that pentanal was converted to pentanoic acid at higher ozone doses. Glyoxal and methyl glyoxal exhibited different behaviors in different batches of OR water. In one, it behaved like pentanal, i.e., observed at lower concentration at higher doses after reaching a maximum (Shukairy et al. 1992). In another, they had not yet reached maximums at 2.8 mg/mg (Miltner et al. 1992). At ozone doses more typical of drinking water treatment (0.5 to 1.5 mg/mg transferred ozone/TOC), concentrations of OBPs are generally increasing; therefore, minimizing the ozone dose can limit OBP formation.
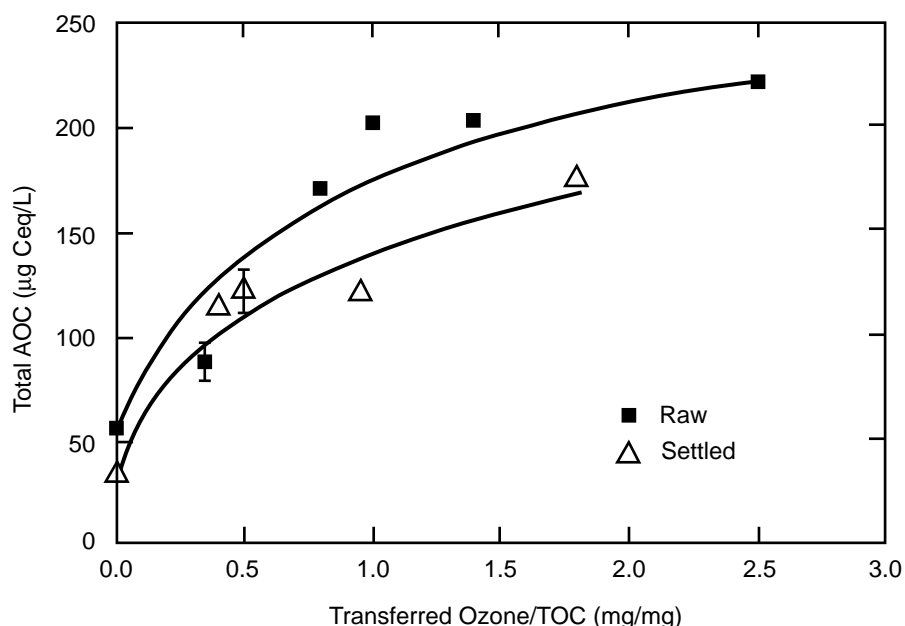
Figure 6-3. Effect of ozone dose on total AOC in OR water (Miltner et al. 1998).

Ozone staging (when it is applied in the treatment plant) can influence OBP formation. Miltner et al. (1998) studied bench-scale ozonation of raw, coagulated and settled OR waters. Raw water was ozonated at a transferred ozone/TOC ratio of 1.4 mg/mg and settled water at a transferred ozone/TOC ratio of 1.1 mg/mg. These were based on oxidation of SUVA and DBP precursors in raw and settled waters and on achieving the concentration and time (CT) required to inactivate approximately 2 logs *Cryptosporidium parvum* oocysts. The inactivation studies treated *C. parvum* oocyst-spiked OR water (Owens et al. 2000). Table 6-14 shows that ozonating settled water resulted in lower concentrations of OBPs than ozonating raw water prior to coagulation and settling. Coagulation removed some of the ozone-reactive NOM. Further, coagulation removed ozone demand such that the inactivation CT requirements could be met at a lower ozone dose (4.7 mg/L [1.4 × 3.35] in the raw water vs. 2.8 mg/L [1.1 × 2.59] in the settled water). The ozone dose dependency of OBP formation was previously discussed. After formation of OBPs in the raw water, OBP removal by coagulation and settling was minimal. It must be noted, however, that at the bench scale, no biological activity took place in the sedimentation process. Miltner and Summers (1992) demonstrated removal of AOC in a pilot-scale, bioacclimated sedimentation basin at room temperature.

Table 6-14. Effect of Ozone Staging on OBPs in OR Water (Miltner et al. 1998)

Parameter	Raw	Settled, then Ozonated (1.1 mg/mg O3/TOC)	Ozonated (1.4 mg/mg O3/TOC), then Settled
TOC, mg/L	3.35	2.59	2.58
Total AOC, µg Ceq/L	142	297	440
Formaldehyde, µg/L	3.0	11.9	31.4
Glyoxal, µg/L	ND	3.9	7.2
Methyl glyoxal, µg/L	ND	9.2	15.2
Glyoxylic acid, µg/L	ND	64.8	189
Pyruvic acid, µg/L	ND	36.3	119

Controlling Bromate

Ozone reacts with bromide to form bromate, and bromate is regulated at 10 µg/L under the D/DBP Rule. While this reaction, or series of reactions, is complex, hypobromite ion is an intermediate product. Thus, minimizing pH to favor hypobromous acid over hypobromite ion is cited as a best available technology (BAT) for bromate control in the D/DBP Rule. Other means of control include adding ammonia to form bromamines in place of the free-bromine (hypobromite and hypobromous acid) species and applying ozone in a manner that minimizes the presence of the dissolved ozone residual driving the reaction.

Bromate formation as a function of increasing bromide concentration was studied by Shukairy et al. (1994) in a pilot-scale ozone contactor treating OR water. Owens et al. (2000) studied inactivation of spiked *Cryptosporidium parvum* oocysts in the same pilot-scale ozone contactor treating different batches of OR water. The pH was in the 7.40 to 7.65 range for the bromate study. The results in Table 6-15 show bromate concentration increasing with increasing dissolved ozone residual and with increasing bromide. With ambient bromide (50.7 µg/L), the bromate MCL was exceeded near a transferred ozone/TOC ratio of 1.1 mg/mg, at which approximately 1.3-log inactivation of *C. parvum* oocysts would occur. At relatively high bromide concentrations, prohibitive bromate concentrations occured at low ozone doses. This pilot-scale contactor was a single, countercurrent chamber. In a full-scale, multi-chamber contactor, the same ozone might be applied over several chambers, minimizing the dissolved ozone driving the bromate reaction, but maintaining the dissolved ozone required for achieving CT.

Table 6-15. Effect of Ozone Dose and Bromide on Bromate Formation in OR Water (Shukairy et al. 1994; Owens et al. 2000)

Trans O_3 mg/L	Trans O_3/DOC mg/mg	Residual O_3 mg/L	CT* mg min/L	Log Inact *C. parvum* Oocysts	Bromate Concentration, µg/L		
					Br^- 50.7 µg/L	Br^- 258 µg/L	Br^- 550 µg/L
0	0	0	0	0	<0.2	<0.2	<0.2
0.89	0.53	0.28	0.96	0.30	1.1	7.6	14.2
1.37	0.81	0.66	2.15	0.72	4.1	25.4	24.4
1.93	1.11	1.16	3.85	1.31	10.5	45.2	58.8
3.02	1.78	2.15	7.18	2.48	24.1	103	145
4.32	2.54	3.27	10.9	3.79	40.7	198	303

*CT = Cavg × T, in which Cavg = 0.45 to 0.5 residual O_3 and T = theoretical = 7.4 min mean

Summary

The formation of halogen-containing DBPs by chloramines is significantly lower than by free chlorine. An exception is the formation of cyanogen chloride with chloramination. The formation of non-halogenated DBPs like aldehydes and AOC is minimal with chloramination.

The formation of halogen-containing DBPs by chlorine dioxide is significantly lower than by free chlorine. ClO_2 oxidizes DBP precursors to the extent that lower concentrations of DBPs are formed with subsequent chlorination. ClO_2 forms non-halogenated DBPs like aldehydes, ketones, and AOC.

Chlorite and chlorate can result from the use of ClO_2. Chlorite can be controlled by GAC and by reducing agents. Sulfite and metabisulfite can reduce chlorite, but may form chlorate. Thiosulfate can reduce chlorite without forming chlorate. Ferrous ion can also reduce chlorate, but pH adjustment is

required to minimize chlorate formation. The use of a reducing agent like thiosulfate or ferrous ion can complicate the application of post-disinfectants.

The formation of halogen-containing DBPs by ozone is significantly lower than by free chlorine. Ozone can form bromo-DBPs like $CHBr_3$, BAA, and DBAA, but at relatively low concentrations. Ozone oxidizes DBP precursors such that lower concentrations of TTHM, HAA6, HAN4, and TOX are formed with subsequent chlorination. However, ozone alters the nature of the precursors to the extent that higher concentrations of CH, CP, and 111-TCP are formed with subsequent chlorination.

Ozone converts portions of the humic fraction to non-humic compounds and converts portions of the higher-molecular-weight fraction to lower-molecular-weight compounds. Examples of lower-molecular-weight materials formed by ozone are aldehydes, keto acids, AOC, and BDOC. Concentrations of these may be appreciable and necessitate control to ensure distribution system biostability. Generally, much of the formation of these OBPs occurs at lower ozone doses. Ozone staging (when it is applied in the treatment plant) can influence OBP formation. Ozonation of raw water results in higher OBP formation than ozonation of downstream waters in which some ozone demand has been removed.

Bromate can result from the use of ozone. Bromate concentration increases with increasing dissolved ozone residual and with increasing bromide.

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